Developing a Perspective for Management of Endocrine Disrupting Compounds in Water Resources

Esra Şıltu[1*], Aybala Koç Orhon[1], Sibel Mine Güçver[1], Bilal Dikmen[1], Yakup Karaaslan[1]

[1]Republic of Turkey, Ministry of Forestry and Water Affairs, General Directorate of Water Management, Ankara, Turkey

[*]e-mail: esiltu@ormansu.gov.tr, +90 312 207 5442

Abstract

The aim of this study is to develop a management perspective for endocrine disruptors in surface waters of Turkey. In this scope, endocrine disruptors having tendency to occur in surface waters were identified. Detailed literature survey was conducted and endocrine disruptors used in Turkey were gathered. These chemicals were monitored in wastewater discharges and water bodies in pilot basins. The fate of these pollutants in aquatic ecosystems was assessed and the chemicals to be regulated in Turkey were designated based on monitoring and fate studies. Environmental quality standards were derived for these chemicals and advanced treatment options were studied.

Introduction:

Endocrine disrupting compounds are of significant interest in water management because of their catastrophic effects on ecosystem and human health. When they enter to body of a living being, they mimic the hormones or interfere with the endocrine system and cause severe health problems. These chemicals are mostly of synthetic origin. Moreover, most of them are very persistent in the environment and exist for many years after the emission. There are many scientific studies proving the adverse effects of endocrine disrupting compounds on both environment and human health (Güven & Öztürk, 2005; Akbulut & Deniz-Yön, 2013; Canesi & Fabbri, 2015; Colborn et al., 1993; Vos et al., 2000). Endocrine disruptors were observed to have significant negative effects on synthesis and segregation of estrogenic, antiestrogenic, androgenic, antiandrogenic and thyroid hormones in human body (Altan, 2000).

The molecular structures of endocrine disrupting chemicals differ widely. These differences complicate the classification of endocrine disrupting chemicals and also result in difficulties in systematic investigations on these chemicals. However, the way they affect the living organisms is mostly similar. The sources of endocrine disrupting chemicals are urban and industrial discharges and agricultural activities. As a result of these activities, the endocrine disrupting chemicals bearing wastewaters reaches to receiving water bodies. Therefore, water is one of the most important routes of exposure to endocrine disrupting compounds. This situation necessitates the control of endocrine disrupting compounds in water resources and it is an urgent policy issue in water management practice.

In Turkey, several endocrine disrupting compounds were listed in national legislation under specific pollutants and priority substances and their environmental quality standards were set. In addition to these, a project has been initiated by Ministry of Forestry and Water Affairs in cooperation with universities to develop a management perspective for endocrine disrupting compounds in water resources. Ministry of Health, Ministry of Environment and Urbanization, Ministry of Food, Agriculture and Livestock, industrial organizations, municipalities and several research institutes were also involved in the project. By the contributions of professionals and academicians from different disciplines, an integrated management perspective was developed for the control of endocrine disrupting chemicals in surface water resources in Turkey.

Methodology:

In scope of the project, complete list of endocrine disrupting compounds which exist in water resources was prepared. For this purpose, literature and endocrine disrupting compounds lists prepared by international organizations and other countries were reviewed and an inventory of chemicals used in industrial facilities and agricultural activities was taken. The main sources considered in this part are listed below:

- National projects on determination of point and diffuse sourced hazardous substances
- National and international legislation
- NORMAN endocrine disruptors list

- US EPA endocrine disruptors list
- DHI endocrine disruptors list
- WHO study on endocrine disruptors
- UNEP report on endocrine disruptor chemicals
- EU Chemicals Agency reports on endocrine disruptor chemicals
- ChemSec SIN list
- TEDX endocrine disruptors list
- Active pharmaceutical ingredients licensed in Turkey

As a result of this study, universe of chemicals was constituted. Further studies were conducted to make a screening on the universe of chemicals. In this respect, a literature review was conducted to find out the chemicals which have endocrine disrupting property or suspected to have endocrine disrupting property. The listed chemicals were also assessed according to their potential to exist in wastewater and environmental fate. Moreover, degradation by-products and metabolites of endocrine disrupting chemicals in the candidate list were investigated via literature review.

Furthermore, monitoring studies were initiated in the pilot basins namely Marmara and Batı Akdeniz basins to detect the levels of these pollutants in both receiving surface water bodies and urban and industrial wastewater discharges. Monitoring studies were conducted in seasonal periods. GC-MS/MS, GC-MS, GC-ECD, LC-MS/MS, ICP-OES, atomic absorption spectrophotometry devices were used for the analysis of endocrine disruptors depending on their physicochemical properties. Prior to analysis, liquid-liquid extraction was applied to samples when needed.

In addition to these, the fate of these chemicals in the water environment was searched in detail from the existing literature. In this sense, the physicochemical properties of these chemicals such as persistency, bioaccumulation potential, water solubility, octanol-water partitioning coefficient, vapour pressure, Henry's law constant, degradation half-life in water environment were gathered. Then, the collected data were assessed to determine the tendency of these chemicals to partition into the water phase by using some partitioning models like Mackay model (Mackay, 2001; Mackay et al., 2006). The outcomes of these assessments were used for the identification of endocrine disrupting chemicals which have significant importance in regard to surface water management.

Another stage of the study was to take a sectorial inventory of the endocrine disrupting chemicals in Turkey. Endocrine disruptors are used in production processes in several different industries and they can be formed as side product or exist in wastewater discharges of industrial facilities (Ministry of Forestry and Water Affairs, 2016). Moreover, they can also be encountered in urban wastewater discharges. The main sources of the endocrine disrupting compounds in Turkey are sectors listed below:

- Urban wastewater discharges/ wastewater treatment plants
- Hospitals and laboratories
- Pesticides production facilities
- Human and veterinary pharmaceutical production facilities
- Chemical production facilities (chemical, plastics, personal care products and cleansing agents)
- Textile and leather industry

- Paint and varnish industry
- Metal industry
- Automotive industry
- Pulp and paper industry
- Packaging industry
- Food industry
- Recycling and recovery facilities
- Landfills
- Refineries and petroleum production facilities
- Agricultural activities

The capacity reports of the plants operating in these sectors in Turkey were analysed and the endocrine disrupting chemicals used or generated in these facilities were identified. In addition to this, literature survey was conducted to find out the endocrine disrupting chemicals used in these manufacturing activities and the list of chemicals produced or imported in Turkey was considered. Also, questionnaires and field studies were carried out in the pilot regions to support the inventory study. The findings of these studies were aggregated to compose the final sectorial inventory of endocrine disrupting chemicals.

Comprehensive studies on treatment of endocrine disrupting chemicals from wastewater discharges were also performed. In this context, both literature review and laboratory scale investigations were carried out. Removal of selected endocrine disrupting compounds via advanced wastewater treatment technologies were examined in lab scale systems.

Following these studies, environmental quality standards for water column, sediment and biota matrices were derived for these pollutants. For deriving environmental quality standards, the methodology defined in European Union Water Framework Directive (2000/60/EC) Common Implementation Strategy Guidance Document No: 27 was followed (European Commission, 2011). In this stage, acute and chronic toxicity data was collected from different databases (EPA, TOXNET etc.) and academic papers for organisms representing three trophic levels namely daphnia magna, algae and fish. Then, the calculations were made by using the deterministic and probabilistic methods described in the guidance document. Deterministic method was applied when the number of reliable and relevant toxicity data from the three trophic levels was lower than ten. In this method, the lowest reliable and relevant toxicity data was taken as a datum and divided by an assessment factor which was determined in the guidance document according to the number and nature of reliable, relevant and available toxicity data. On the other hand, probabilistic method which is also known as species sensitivity distribution method was applied when there is satisfactory number of reliable, relevant and available toxicity data. In this method, ETX software was used for the calculations and HC5 value which is the hazard concentration protecting almost 95 % of the population of species that are most sensitive to the corresponding chemicals was calculated (European Commission, 2011). ETX software makes use of a statistical model for the calculation of HC5 value. Following the calculation of HC5 value, the calculated value was divided by an assessment factor described in the guidance document. The assessment factors used in the deterministic method were higher than the assessment factors used in the probabilistic method. Therefore, the probabilistic

method yielded more applicable and realistic environmental quality standards for the chemicals as compared to deterministic method when there was satisfactory number of reliable, relevant and available toxicity data. Hence, the probabilistic method was preferred in this study most of the time if the necessary data was collected.

In order to determine whether the sediment environmental quality standards should be calculated or not, logarithm of octanol-water partitioning coefficient of chemicals were checked. If the logarithm of octanol-water partitioning coefficient was greater than 3, the sediment environmental quality standards were derived. For biota environmental quality standards, bioconcentration factors and biomagnification factors were checked firstly. If these two values were not available, logarithm of octanol-water partitioning coefficient was checked. If the bioconcentration factor was greater than 100 and biomagnification factor was greater than 1 for a chemical, then the biota environmental quality standards were calculated. For logarithm of octanol-water partitioning coefficient, the same criterion was valid.

Results and Discussions:

As a result of this study, universe of chemicals including 7254 candidate endocrine disruptor chemicals was constituted as described in methodology part. The sources of these chemicals are shown in Table 1.

Table 1: Constitution of universe of chemicals

Source	**Number of chemicals**
TMKK Project	2991
KIYITEMA Project	3378
BIKOP Project	474
National legislation	299
NORMAN	965
EPA	181
EU (2000,2002)	549
EU(2006)	316
WHO	181
UNEP	90
REACH	200
SIN	71
TEDX	1052
CoRAP	322
Active pharmaceutical ingredients	55
Other countries	137
National studies	447
Drinking water legislation	109
Güzel (2015)	92
Substances monitored in	87

drinking waters	
TOTAL	**7254**

Further studies were conducted to make a screening on the universe of chemicals. In this respect, a literature review was conducted to find out the chemicals which have endocrine disrupting property or suspected to have endocrine disrupting property. At the end of this study, 1000 chemicals were observed to have endocrine disrupting property and 902 chemicals were observed as suspected endocrine disruptors. The sources of chemicals in the candidate list are represented in Table 2.

Table 2: Constitution of candidate endocrine disrupting chemicals list

Source	Number of endocrine disrupting chemicals	Number of suspected endocrine disrupting chemicals
TMKK Project	742	78
KIYITEMA Project	728	108
BIKOP Project	156	136
National legislation	140	70
NORMAN	158	106
EPA	11	6
EU (2000,2002)	233	159
EU(2006)	191	0
WHO	91	48
UNEP	82	0
REACH	40	19
SIN	66	1
TEDX	262	788
CoRAP	32	35
Active pharmaceutical ingredients	5	3
Other countries	51	35
National studies	167	78
Drinking water legislation	1	1
Güzel (2015)	35	20
Substances monitored in drinking waters	55	26
TOPLAM	**1000**	**902**

The candidate endocrine disruptors list consists of 1902 chemicals from different groups like pesticides, PAHs, PCBs, PCDD/Fs, phthalates, phenols, metals and

metallic compounds and pharmaceuticals. The well-known endocrine disrupting chemicals in these groups are listed in Table 3:

Table 3: Groups of endocrine disruptors in the candidate list (WHO, 2012)

Persistent and Bioaccumulative Halogenated Chemicals	
Persistent Organic Pollutants (POP)	PCDD/PCDFs, PCBs, HCB, PFOS, PBDEs, PBBs, Chlordan, Mirex, Toxaphene, DDT/DDE, Lindane, Endosulfan
Other persistent and bioaccumulative chemicals	HBCDDs, SCCP, PFCAs (PFOA), Octachlorostyrene, methylsulfanes
Less Persistent and Less Bioaccumulative Chemicals	
Plasticizers and additives	Phytalate esters (DEHP, BBP, DBP, DiNP), Triphenyl phosphate, Bis(2-ethylhexyl)adipat, n-Buthylbenzene, Triclocarban, Buthylated hydroxyanisole
PAH	Benzo(a)pyrene, Benzo(a)anthracene, Pyrene, Anthracene
Halogenated phenolic compounds	2,4-Dichlorophenol, Pentachlorophenol, Hydroxy-PCBs, Hydroxy -PBDEs, Tetrabromobisphenol A, 2,4,6-Tribromophenol, Triclosan
Non-halogenated phenolic compounds (Non-HPCs)	Bisphenol A, Bisphenol F, Bisphenol S, Nonylphenol, Octylphenol, Resorcinole
Active Ingredients in Pesticides, Pharmaceuticals and Personal Care Products	
Pesticides in use	2,4-D, Atrazine, Carbaryl, Malathion, Mancozeb, Vinclozolin, Prochloraz, Procymidone, Chloropyrifos, Fenitrothion, Linuron
Additives in pharmaceuticals and personal care products	Active endocrine (Diethylstilbestrol, Ethinylestradiol, Tamoxiphene, Levonorgestrel), SSRIs (i.e. Fluoxetin), Flutamide, 4-Methybenzylidene camphor, Octyl-methoxicinnamate, Parabens, Cyclic methyl ciloxan (D4, D5, D6), Galaxolide, 3-Benzilidin camphor
Other Chemicals	
Metals and Organometalic Compounds	Arsenic, Cadmium, Lead, Mercury, Methyl mercury, Tributhyltin, Triphenyltin
Natural hormons	17β-estradiol, Estron, Testosteron
Fitoestrogenes	Izoflavon (Jenistein, Daidzein), Coumestans (Coumestrol), Mikotoxin (Zearalenone), Prenylflavonoids (8-prenylnaringenin)

The fate of endocrine disrupting chemicals in water ecosystems and their effect mechanisms on organisms depends on the physicochemical properties of these chemicals like octanol-water partitioning coefficient, bioaccumulation factor and

environmental conditions like temperature, pH and salinity (Lapworth et al., 2012). According to the specific circumstances, the chemicals may sorb to sediments or benthic layers in water environment or they can partition to the suspended materials in water. By this way, endocrine disrupting chemicals stays in the water environment without undergoing degradation for months or even years long. Aquatic organisms may be exposed to these chemicals through feeding or absorption. Chemicals adsorbed onto the sediments pose a significant risk to benthic organisms and they accumulate in the food web. On the other hand, some of the chemicals degrade easily biologically or by photolysis or chemical processes. Fishes are exposed to soluble endocrine disrupting chemicals through their gills while birds and mammals are exposed through drinking water consumption.

The partitioning behaviour of the chemicals affects the bioavailability in aquatic ecosystems and hence this mechanism is of significant importance for managing and regulating the endocrine disrupting chemicals reaching to surface water resources. By considering the fate of candidate endocrine disrupting substances (i.e. 1902 chemicals), a more strict screening and prioritization were applied on the list and final list of endocrine disrupting chemicals relevant for water management was obtained.

The endocrine disrupting chemicals listed in final list was monitored in Batı Akdeniz and Marmara pilot basins. Marmara Basin was selected due to heavy industrial activities which represents all the manufacturing activities in Turkey. There are many industrial facilities in Marmara Basin from different sectors like pulp and paper, textile, chemicals, metal, food, pharmaceuticals, petroleum production and cosmetics. On the other hand, Batı Akdeniz Basin was selected due to the widespread agricultural and tourism activities. In these pilot river basins, both wastewater discharges and surface waters were monitored in terms of levels of endocrine disrupting chemicals. In the analysis, measurements in ng/L levels were achieved. The outcomes of the monitoring studies demonstrated that the levels endocrine disrupting substances were below the allowable limits in surface waters of Turkey. However, it was observed that there is a need for further treatment of the endocrine disrupting compounds from some of the urban and industrial wastewater treatment plants in the pilot river basins.

By considering the monitoring results and fate of chemicals in the surface water environment, final list of endocrine disrupting chemicals was revised accordingly. The chemicals which have potential to occur in wastewaters and water resources were taken into consideration in the revision process. For the chemicals originating from point sources, sectorial inventory was taken. For the diffuse sourced pesticides which were present in the revised final list, an inventory based on agricultural product pattern was constituted. Furthermore, environmental quality standards in water column, sediment and biota were derived for those endocrine disrupting compounds. The calculated environmental quality standard values were assessed by comparing to the environmental quality standards derived by other countries and also to the limit of detection and quantification values of the analytical methods used. By this way, the endocrine disrupting chemicals that should be regulated and their environmental quality standards for fresh and marine waters were designated on national basis.

The existence of endocrine disrupting compounds in the wastewaters made the research on the advance treatment of endocrine disruptors essential. In this respect, firstly the fate of endocrine disruptors in the wastewater treatment systems was analysed and actual removal efficiencies of the existing treatment plants were put forth. It was shown that these chemicals can be converted to more hazardous compounds, less hazardous by-products or completely degraded to simple inorganic compounds in the wastewater treatment system or they can be adsorbed to the sewage sludge due to their hydrophobic property or they can be directly discharged to receiving water bodies without underdoing any degradation. Following the investigation of these fate mechanisms in wastewater treatment systems, revision requirements were determined and advanced treatment technologies such as ozonation, activated carbon, phenton oxidation and membrane systems were simulated in the laboratory scale experiments. In this laboratory scale experiments, wastewaters samples from pharmaceutical industry, organized industrial zone and urban wastewater treatment plant effluents were used. The results showed that these technologies can reach removal efficiencies up to 70%-99.9% depending on the characteristics of raw wastewaters and physical conditions. However, in order to achieve these removal efficiencies in conventional treatment plants, the systems must be optimized to favour the degradation of endocrine disrupting chemicals together with other substrates. Moreover, it should be noted that the degradation by-products of the endocrine disrupting compounds may be even more persistent and bioaccumulative in aquatic ecosystems.

Conclusions:

In scope of the project, complete list of endocrine disrupting compounds which exist in water resources was prepared. For this purpose, literature and endocrine disrupting compounds identified by international organizations and other countries were reviewed and an inventory of chemicals used in industrial facilities and agricultural activities was taken. The listed chemicals were assessed according to their potential to exist in wastewater and water environment and environmental fate. Then, environmental quality standards were derived in water column, sediment and biota for these pollutants. Moreover, monitoring studies were conducted to detect the levels of these pollutants in both receiving water bodies and wastewater discharges in Batı Akdeniz and Marmara Basins.

In addition to these, the fate of these chemicals in the water environment was researched and removal of selected endocrine disrupting compounds via advanced wastewater treatment technologies such as ozonation, activated carbon, phenton oxidation and membrane systems were investigated in lab scale systems.

As a result of this study, a roadmap and a perspective were developed for Turkey to manage the endocrine disrupting pollutants in surface water resources in all 25 river basins. The outputs of the study are planned to be integrated to the national legislation and necessary measures will be implemented by related institutions and organizations. Thereby, the regulation process was governed by the outputs and findings of scientific studies. With these features, the study exhibits a good example of harmonization of scientific efforts with the policy making procedure. It also ensures the implementation of measures by involving all the stakeholders from the beginning of the process.

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